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## Solid-state Synthesis of Cobalt Germanides in Epitaxial Ge/ $\alpha$ -Co(001) and Ge/ $\beta$ -Co(110) Nanofilms

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*The experimental results of a study of solid-state synthesis of cobalt germanides in epitaxial Ge/ $\alpha$ -Co(001) and Ge/ $\beta$ -Co(110) nanofilms are presented. For both polymorphic modifications of cobalt, it is demonstrated that the Co<sub>5</sub>Ge<sub>7</sub> phase occurs at  $\sim 275^\circ\text{C}$ . When the annealing temperature increases to  $\sim 300^\circ\text{C}$ , the CoGe<sub>2</sub> phase forms, which sharply reduces the electric resistance and magnetic characteristics of the samples. The order of the formation of phases and the temperatures at which the phases are formed are not changed based on the polymorphic modification of cobalt.*

*Keywords: epitaxial growth, nanofilms, solid-state synthesis, Co-Ge system, cobalt germanides.*

Studying the chemical interactions between the metals with various semiconductors has shown that the interface acquires new structural and magnetic properties. Chemical reactions on the interface of the films often cause solid-state reactions, which are in the focus of intensive research. The main efforts of this research are focused on studying the formation of silicides on the interface of metallic films with silicon [1]. To a lesser extent, there has been some research of solid-state reactions of metals with germanium. Most studies [2–4] show that as the annealing temperature increases, the Co<sub>5</sub>Ge<sub>7</sub> phase on the Co/Ge interface occurs first at a temperature

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of  $\sim 300^\circ\text{C}$ , and then changes into the  $\text{CoGe}_2$  phase at a temperature of  $\sim 425^\circ\text{C}$ . In some works though [5], it is shown that the  $\text{CoGe}$  phase forms first on the  $\text{Co/Ge}$  interface, and then as the annealing temperature increases the phases follow the following order:  $\text{Co/Ge} \rightarrow \text{CoGe} \rightarrow \text{Co}_5\text{Ge}_7 \rightarrow \text{CoGe}_2$ . A structural analysis of thin films of  $\text{Co}$  growing on  $\text{Ge}(111)$  and  $\text{Ge}(001)$  using photoelectric X-ray diffraction and low-energy electron diffraction, has shown a mixing of  $\text{Co}$  and  $\text{Ge}$  at a low temperature ( $\sim 100^\circ\text{C}$ ) and a possible formation of the first  $\text{CoGe}_2$  phase [6]. The results of photoelectric investigations show a mixing of the layers on the interface between  $\text{Co}$  and  $\text{Ge}(100)$  at a very low ( $\sim 170\text{ K}$ ) temperature [7]. The  $\text{CoGe}_2$  and  $\text{CoGe}$  phases have very low symmetry, and only  $\text{Co}_5\text{Ge}_7$  has a tetragonal lattice and grows epitaxially between other phases on  $\text{Ge}(111)$  and  $\text{Ge}(100)$  surfaces in an ultrahigh vacuum [5, 6]. The chemical reactions and epitaxial growth of  $\text{Ge}$  on various  $\beta\text{-Co}$  and  $\alpha\text{-Co}$  surfaces have not been investigated.

It is well known that bulk samples of the hexagonal  $\alpha\text{-Co}$  phase are stable at temperatures below the allotropic  $\alpha \leftrightarrow \beta$  transformation. But small samples and thin films of the  $\alpha\text{-Co}$  phase are often stable at room temperature. This paper reports the findings on solid-phase reactions on the interface between metastable cubic  $\beta\text{-Co}(001)$  and hexagonal  $\alpha\text{-Co}(110)$  films with a polycrystalline  $\text{Ge}$  layer.

Initial  $\text{Ge}/\beta\text{-Co}(001)$  and  $\text{Ge}/\alpha\text{-Co}(110)$  film structures were made using thermal evaporation on a monocrystalline  $\text{MgO}(001)$  substrate in a vacuum of  $10^{-5}$  torr. Samples with an atomic ration close to  $3\text{Ge}:2\text{Co}$  were used in these experiments. The thickness of the films used was not more than  $300\text{ nm}$ . In order to prevent a solid-state reaction between  $\text{Ge}$  and  $\text{Co}$ , the  $\text{Ge}$  film was precipitated at room temperature. The resulting samples were annealed in a vacuum of  $10^{-5}$  torr over  $25^\circ\text{C}$  for 20 minutes at temperatures between  $100^\circ\text{C}$  and  $350^\circ\text{C}$ . X-ray investigations using a DRON-4-07 diffractometer ( $\text{Cu } K_\alpha$  — radiation) were used to identify the formed phases. Fluorescent X-ray was used to identify the chemical composition and thickness of the films. Measurements of the magnetic crystallographic anisotropy and the saturation of magnetization were made using the method of torsional moment in a maximum magnetic field of  $18\text{ kOe}$ . All measurements were made at room temperature.

In order to get epitaxial  $\beta\text{-Co}(001)$  layers, cobalt was precipitated at a temperature of  $\sim 250^\circ\text{C}$ . A strong and singular diffractive reflection of  $(002)$   $\beta\text{-Co}$  confirms the formation of an epitaxial  $\beta\text{-Co}(001)$  layer (Fig. 1a). Each sample had a biaxial magnetic anisotropy with a constant of  $K_2 = -(6.0 - 7.0) \cdot 10^5 \text{ erg/cm}^3$ . The light axis of magnetization of  $\beta\text{-Co}$  film coincides with the direction of  $[110]$  and  $[1-10]$  of the substrate  $\text{MgO}(001)$ , which indicates the presence of orientational correlation  $[100](001)\beta\text{-Co} \parallel [100](001)\text{MgO}$  during epitaxial growth of cubic cobalt on the surface of  $\text{MgO}(001)$ . These two factors indicate a crystalline perfection of the initial  $\beta\text{-Co}(001)$  layers, acquired in the given technological conditions.

The epitaxy of  $\text{Co}$  on the surface of  $\text{MgO}(001)$  radically changes when precipitation occurs at temperatures of  $\sim (370-400)^\circ\text{C}$ . The diffraction patterns of the samples show that  $\alpha\text{-Co}$  crystalline particles  $(110)$  grow on  $(001)$  the surface of  $\text{MgO}$  (Fig. 2a). The analysis performed in the work [8] shows that  $\alpha\text{-Co}(110)$  crystalline particles grow on  $\text{MgO}(001)$  following two epitaxial ratios:  $\alpha\text{-Co}(110)[001] \parallel \text{MgO}(001)[110]$  and  $\alpha\text{-Co}(110)[100] \parallel \text{MgO}(001)[1-10]$ . The constant  $K_{eff}$  of effective biaxial magnetic anisotropy of  $\alpha\text{-Co}(110)/\text{MgO}(001)$  films is  $K_{eff} = (1.1-1.2) \cdot 10^6 \text{ erg/cm}^3$ . The energy of magnetic anisotropy  $E_K$  of a hexagonal crystal (without taking into account the anisotropy in the plane of the film) is  $E_K = K_1 \sin^2 \varphi + K_2 \sin^4 \varphi + \dots$  for  $\alpha\text{-Co}$ , where  $K_1 = 4.3 \cdot 10^6 \text{ erg/cm}^3$ ,  $K_2 = 1.2 \cdot 10^6 \text{ erg/cm}^3$  and  $\varphi$  is the angle between the axis  $\mathbf{c}$  and the direction of magnetization  $M_S$  [19]. Assuming that the crystalline particles  $\alpha\text{-Co}(110)$ , growing along the axis  $\mathbf{c}$  in the directions  $[110]$  and  $[1-10]$   $\text{MgO}$ , are interchangeable and all have

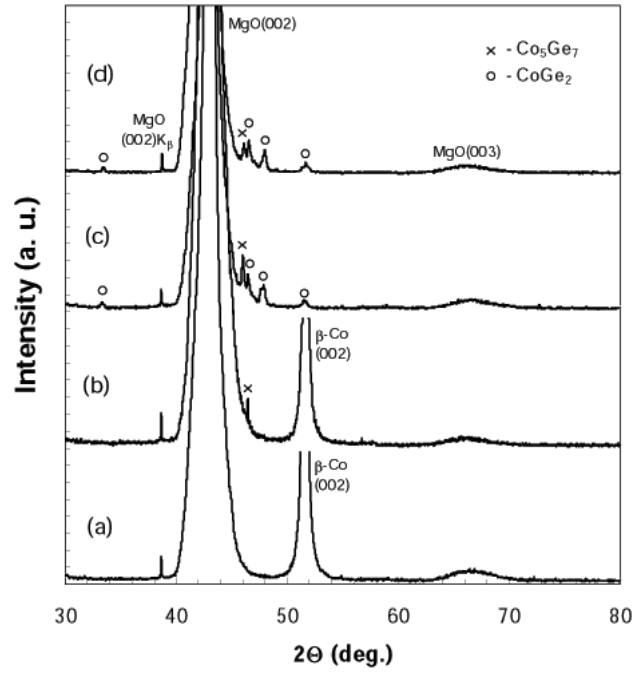


Fig. 1. Diffraction patterns of Ge/ $\beta$ -Co(001) films after annealing: (a) at 20 °C, (b) at 275 °C, (c) at 300 °C, (d) at 350 °C

the same volume, the constant  $K_{eff} = K_2$  [9]. The fact that the experimental values of  $K_{eff}$  and  $K_2$  are the same confirms the epitaxial growth of  $\alpha$ -Co(110) crystalline particles on the surface of MgO(001).

The graphs of the constant of biaxial magnetic anisotropy  $K_2$ , the saturation of magnetization  $M_S$  and the electric resistance  $R$  as a function of the annealing temperature  $T_S$  for Ge/ $\beta$ -Co(001) and Ge/ $\alpha$ -Co(110) nanofilms all have the same form taking into account experimental uncertainties. Fig. 3 shows graphs of the constant of biaxial magnetic anisotropy  $K_2$ , the saturation of magnetization  $M_S$  and the electric resistance  $R$  as a function of the annealing temperature  $T_S$  for the given samples. Up until a temperature of 250 °C the values of  $K_2$  and  $M_S$  are not related to  $T_S$ , which indicates that no mixing or formation of connections has occurred on the interface between germanium and cobalt. At temperatures around 275 °C the values of  $K_2$  and  $M_S$  for the monocrystalline cobalt layer decreased for all samples and at a temperature of 300 °C all samples became completely nonmagnetic. At temperatures  $T_S > 300$  °C the values of  $K_2$  and  $M_S$  become zero. This suggests a full mixing of the Co and Ge layers and the synthesis of nonferromagnetic cobalt germanides.

The diffraction patterns change based on the relationships of  $K_2(T_S)$  and  $M_S(T_S)$ . Fig. 1 shows the X-ray spectrum for Ge/ $\beta$ -Co(001) nanofilms at their initial temperatures and after annealing at temperatures of 275 °C, 300 °C and 350 °C. After annealing at a temperature of 275 °C, the diffractational reflection for (002) $\beta$ -Co decreased and new weaker peaks formed, which indicates a formation of polycrystalline phases as a product of the reactions (Fig. 1b). The diffractational reflections for many of the phases of the Co-Ge films are the same, but the reflection when  $2\theta = 45.8^\circ$  can only come from a peak of the (222) $\text{Co}_5\text{Ge}_7$  phase. This suggests that the  $\text{Co}_5\text{Ge}_7$  phase forms first on the Ge/ $\beta$ -Co(001) interface at a temperature of 275 °C. At a

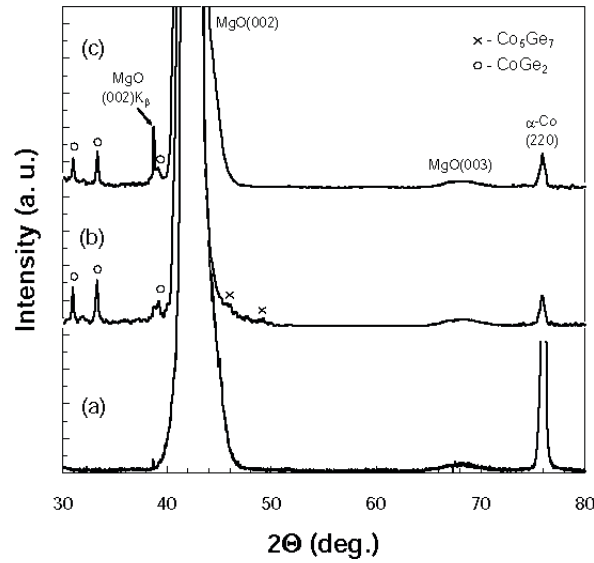


Fig. 2. Diffraction patterns of Ge/ $\alpha$ -Co(110) films after annealing: (a) at 20 °C, (b) at 300 °C, (c) at 350 °C

temperature of 300 °C the reflection from (002) $\beta$ -Co disappears, but the peak from (222) $\text{Co}_5\text{Ge}_7$  grows, which indicates a further increase in volume for this phase (Fig. 1c). The reflection from the  $\text{CoGe}_2$  orthorhombic phase also appears at this temperature. At a temperature of 350 °C the peak from (222) $\text{Co}_5\text{Ge}_7$  decreases and the  $\text{Co}_5\text{Ge}_7$  phase turns into the  $\text{CoGe}_2$  phase, which becomes the dominant product in the reactions (Fig. 1d).

As shown by the decrease of the constant of biaxial magnetic anisotropy  $K_2(T_S)$  and by the decrease of the saturation of magnetization  $M_S(T_S)$ , the solid-state reaction in Ge/ $\alpha$ -Co(110) nanofilms, just like in the Ge/ $\beta$ -Co(001) nanofilms, starts at a temperature of 275 °C. But there are no new reflections on the diffraction patterns, which might indicate the formation of a new phase that has a disordered finely-dispersed structure. The diffraction patterns after annealing at a temperature of 300 °C show reflections that belong to the  $\text{CoGe}_2$  and  $\text{Co}_5\text{Ge}_7$  phases (Fig. 2b). The weak peak from (222) $\text{Co}_5\text{Ge}_7$  disappears from the diffraction pattern after annealing at a temperature of 350 °C, which suggests a decrease of the  $\text{Co}_5\text{Ge}_7$  phase in the products of the reaction (Fig. 2c). Only the reflections from the  $\text{CoGe}_2$  phase remain after annealing at a temperature of 350 °C, so the transformation of the (222) $\text{Co}_5\text{Ge}_7$  peak is the same for both the Ge/ $\alpha$ -Co(110) and the Ge/ $\beta$ -Co(001) nanofilms. This suggests that the disordered finely-dispersed  $\text{Co}_5\text{Ge}_7$  phase in the Ge/ $\alpha$ -Co(110) nanofilms also forms at a temperature of 275 °C and precedes the formation of the  $\text{CoGe}_2$  phase. An analysis of the above mentioned facts suggest that the order of the formation of phases in the Ge/ $\alpha$ -Co(110) and Ge/ $\beta$ -Co(001) nanofilms is the same.

The average size of the  $\text{Co}_5\text{Ge}_7$  and  $\text{CoGe}_2$  crystalline particles was determined from the diffraction pattern peaks using Sherrer's formula. For the Ge/ $\beta$ -Co(001) and Ge/ $\alpha$ -Co(110) samples, the average size of the crystalline particles was 17–30 nm.

One of the stages of a solid-state reaction is the breaking of chemical bonds in the reactants. The energy of the bonds in  $\alpha$ -Co is almost the same as the energy of the bonds in  $\beta$ -Co, since the enthalpy of the  $\Delta H^{\beta \rightarrow \alpha} = -220$  cal/mole transition  $\beta$ -Co  $\rightarrow$   $\alpha$ -Co is small. This shows

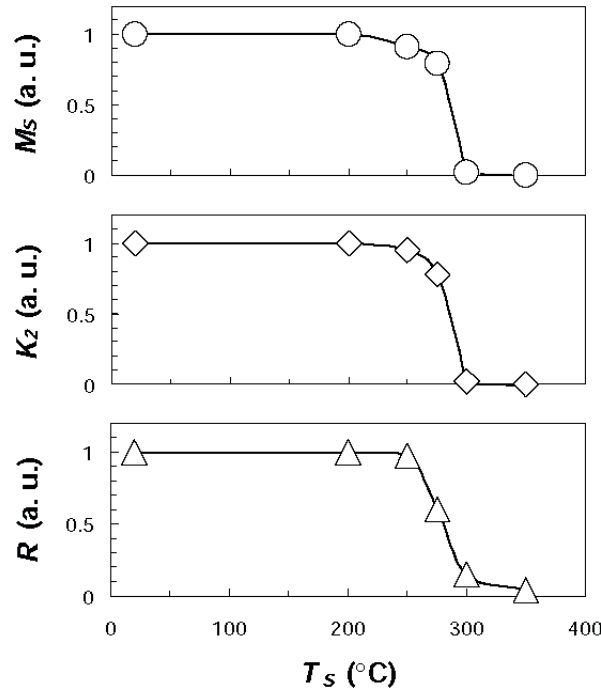


Fig. 3. Saturation of magnetization  $M_S$ , magnetic anisotropy constant  $K_2$ , electric resistance  $R$  of the epitaxial Ge/ $\beta$ -Co(001) and Ge/ $\alpha$ -Co(110) nanofilms as a function of the annealing temperature  $T_S$

that small differences in the energies of the polymorphous reactants does not have an effect on the behavior of solid-state synthesis. In most cases, the enthalpy of the transition from the amorphous phase to the crystalline phase is  $\sim 1000$  cal/mole. Because of this, regardless of whether amorphous, polycrystalline or monocrystalline reactants are used, the order of formation of phases and the temperatures at which each phase forms are the same.

This study shows that annealing polycrystalline Ge nanofilms, precipitated on epitaxial  $\beta$ -Co(001) and  $\alpha$ -Co(110) surfaces, leads to the formation of finely-dispersed polycrystalline  $\text{Co}_5\text{Ge}_7$  and  $\text{CoGe}_2$  phases at temperatures of  $T_0^1 \sim 275^\circ\text{C}$  and  $T_0^2 \sim 300^\circ\text{C}$ , respectively. Small differences in the energies of the polymorphous  $\beta$ -Co and  $\alpha$ -Co modifications of cobalt do not have an effect on the order of formation of phases and the temperatures at which each phase forms.

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## Твердофазный синтез германидов кобальта в эпитаксиальных $\text{Ge}/\alpha\text{-Co}(001)$ и $\text{Ge}/\beta\text{-Co}(110)$ нанопленках

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Представлены экспериментальные результаты исследования твёрдофазного синтеза германидов кобальта в эпитаксиальных  $\text{Ge}/\alpha\text{-Co}(001)$  и  $\text{Ge}/\beta\text{-Co}(110)$  нанопленках. Показано, что для обеих полиморфных модификаций кобальта фаза  $\text{Co}_5\text{Ge}_7$  формируется первой при температуре  $\sim 275^\circ\text{C}$ . С увеличением температуры отжига при температуре  $\sim 300^\circ\text{C}$  образуется фаза  $\text{CoGe}_2$ , которая резко уменьшает электрическое сопротивление и намагниченность образцов. Различные полиморфные модификации кобальта не изменяют последовательность формирования фаз и их температур инициирования.

Ключевые слова: эпитаксиальный рост, нанопленки, твердофазный синтез, Co-Ge система, германиды кобальта.